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The Chemistry of Compounds Containing
Metal-to-Metal Triple Bonds Between
Molybdenum and Tungsten

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The preparation, properties, structures, dynamical solution behaviors and reactivities towards small unsaturated molecules (CO_2, acetylenes, CO, etc.) are described for a series of molybdenum and tungsten compounds of general formula M_2X_6 or $M_2X_{6-n}Y_n$, where $X,Y=R$ (alkyl), NR_2, OR, O_2CNR_2, O_2COR or halide, and $Cp_2M_2(CO)_4$, all of which contain triple bonds between the metal atoms (M=Mo or W).

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Introduction

The recognition that the anion $Re_2Cl_8^{2-}$ contains a rhenium-to- rhenium quadruple bond[1,2] and the rapidly following discoverey of other quadruple M-M bonds constituted a turning point in transition metal chemistry: it raised questions which were previously inconceivable. Aside from obvious questions as to the electronic structure and the propensity of transition metals to form quadruple bonds,[3] there were also broader implications. For example, the existence of a compound containing an M-M bond of order four implied the probable existence of compounds containing M-M multiple bonds of lower order, namely two and three, though few of the former and none of the latter were known at that time. It also suggested that one might speculate on the ability of metals to form M-M multiple bonds of even higher order such as five and six.[4]

This account traces the emergence of a new class of compounds of formula M_2X_6, where X = R(alkyl), NR_2 and OR, which contain metal-to-metal triple bonds (M=Mo and W) unsupported by bridging ligands.[5] It also deals with the organometallic compounds $Cp_2M_2(CO)_4$ (M=Cr, Mo, W), which on the basis of short metal-metal distances (Mo-Mo = 2.40 Å[6]) relative to those in the precursor compounds $Cp_2M_2(CO)_6$ (Mo-Mo = 3.27 Å[7]) and the attainment of the inert gas structure by the metals, may be considered to have metal-to-metal triple bonds.

Certain aspects of the structural and dynamical solution behavior of these compounds, in addition to a number of interesting reactions, warrant specific attention. It seems that organometallic reaction schemes evolved for mononuclear transition metal chemistry may be extended to these dinuclear systems and, furthermore, that these dinuclear compounds may provide building blocks for the systematic syntheses of new polynuclear and cluster

compounds. Both of these considerations have important catalytic implications.[8,9] In an earlier account, the theoretical treatment of these triple bonds was discussed.[10] In this paper we deal entirely with experimental studies of structure, dynamics and reactions.

Syntheses

$\underline{M_2X_6}$ Compounds (X=R,NR_2,OR) The first member of this series $Mo_2(CH_2SiMe_3)_6$ was discovered serendipitously by Wilkinson and his coworkers[11] as a product formed in the reaction of $MoCl_5$ with five equivalents of $LiCH_2SiMe_3$. Analogous reactions involving $MoCl_5$ and $LiNR_2$(5 equiv.) lead to mononuclear $Mo(NR_2)_4$[12] and dinuclear $Mo_2(NR_2)_6$[13-15] compounds (R=Me, Et) which may be separated by fractional sublimation. However, a better route to $Mo_2(NR_2)_6$ involves the reaction between the polymeric $MoCl_3$ and $LiNR_2$ (3 equiv.); only a trace of $Mo(NR_2)_4$ is formed in these reactions.[15]

Some similar reactions involving tungsten halides and organo-lithium reagents are summarized in 1 through 7 below.

$\underset{\sim}{1}$[11] $WCl_6 + 6Me_3SiCH_2Li \rightarrow W_2(CH_2SiMe_3)_6$

$\underset{\sim}{2}$[16-18] $WCl_4 + 4Me_3SiCH_2Li \rightarrow W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$

$\underset{\sim}{3}$[19-21] $WCl_6 + 6LiNMe_2 \rightarrow W(NMe_2)_6 + W_2(NMe_2)_6$

$\underset{\sim}{4}$[21,22] $WCl_4 + 4LiNMe_2 \rightarrow W_2(NMe_2)_6$

$\underset{\sim}{5}$[21] $WBr_5 + 5 LiNMe_2 \rightarrow W(NMe_2)_6$

$\underset{\sim}{6}$[21] $WCl_4(OEt_2)_2 + 4LiNMe_2 \rightarrow W(NMe_2)_6$

$\underset{\sim}{7}$[21,23] $WCl_6 + 6LiNEt_2 \rightarrow W(NEt_2)_2(NEt)_2 + W_2(NEt_2)_6$
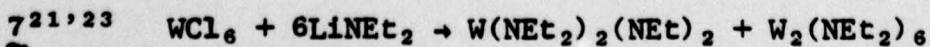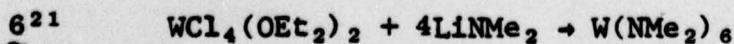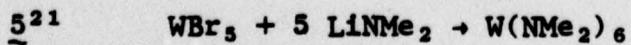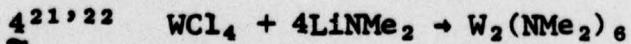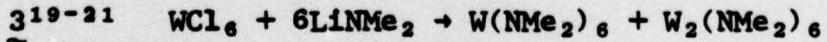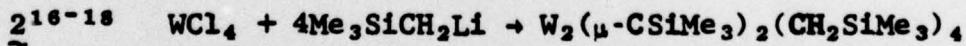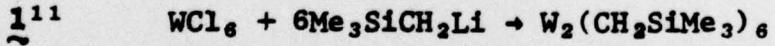
The products depend on the choice of tungsten halide in a manner not yet understood. The reaction pathway leading to the dinuclear compounds $W_2X_6(X=R,NR_2)$ is evidently complex. Neither $Mo(NMe_2)_4$ nor $W(NMe_2)_6$ appear to be precursors for $M_2(NMe_2)_6$, and there is evidence that the $M_2(NMe_2)_6$ compounds are not formed by the coupling of two reactive $M(NMe_2)_3$ units.[24]

Despite the enigmas associated with these metathetic reactions the crystalline compounds $M_2X_6(Mo=Mo,W$ and $X=R,NR_2)$ may be prepared on a large scale and are thus themselves useful starting materials. The dimethylamides react with alcohols and trialkylsilanols to give compounds of empirical formula $Mo(OR)_3$. For molybdenum a fairly extensive series of dinuclear alkoxides $Mo_2(OR)_6(R=Bu^t$, $PhMe_2C$, Me_2CH and $Me_3CCH_2)$ and trialkylsiloxides $Mo_2(OSiR_3)_6(R=Me,Et)$ have been isolated.[13,25] Less bulky alkoxy-ligands give polynuclear compounds, such as, the ethoxide which is tetrameric in benzene. A similar situation holds for tungsten although polynuclear complexes are more common[22,25,28]

$M_2X_{6-n}Y_n$ Compounds In an attempt to establish a much more general class of dinuclear compounds of general formula $M_2X_{6-n}Y_n$, where X and Y are uninegative ligands we sought ways in which to replace M-NR$_2$ groups by M-Cl groups and discovered a very smooth and efficient route,[28] eq. 8. The chloro-for-dimethylamido group

8      $M_2(NMe_2)_6 + 2MeSiCl \rightarrow M_2Cl_2(NMe_2)_4 + 2Me_3SiNMe_2$
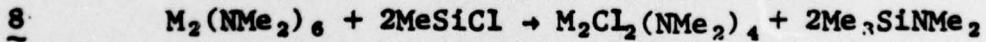
exchange proceeds via an amine catalyzed sequence, eq. 9.

(i) $Me_2NH + Me_3SiCl \rightleftharpoons Me_3SiNMe_2 + HCl$

9 (ii) $M_2(NMe_2)_6 + HCl \rightleftharpoons M_2(NMe_2)_5Cl + HNMe_2$

(iii) $M_2(NMe_2)_6 + M_2Cl_2(NMe_2)_4 \rightleftharpoons 2M_2Cl(NMe_2)_5$; $K\sim1$, $30°C$.
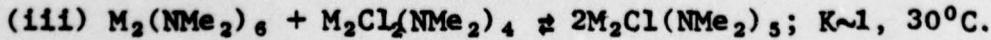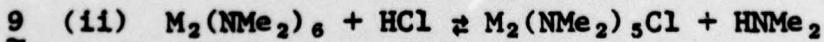
Although other $M_2Cl_x(NMe_2)_{6-x}$ compounds are formed in the reactions between $M_2(NMe_2)_6$ and Me_3SiCl none have been isolated in a pure state. It appears that continued Cl-for-NMe_2 group exchange leads to polymeric rather than dinuclear compounds.

The M-Cl bonds in $M_2Cl_2(NR_2)_4$ compounds (R=Me or Et) are labile to a large number of metathetic reactions. With alkyl-lithium reagents $M_2R_2(NEt_2)_4$ compounds have been isolated with R =Me, Et, n-Bu and CH_2SiMe_3.[29-32] Attempts to prepare $M_2R(Cl)(NEt_2)_4$ compounds failed; presumably because the second R for Cl substitution proceeds faster than the first.[30]

$M_2(NR_2)_6$ and $M_2X_2(NR_2)_4$ compounds are susceptible to a number of the M-N insertion reactions typical of mono-nuclear dialkylamides.[33] With CO_2, $W_2(NMe_2)_6$ gives $W_2(O_2CNMe_2)_6$[34,36] while $Mo_2(NMe_2)_6$ yields only $Mo_2(NMe_2)_2(O_2CNMe_2)_4$.[37] The latter is believed to adopt a structure akin to that of $W_2Me_2(O_2CNEt_2)_4$ which is formed in the reaction between CO_2 and $W_2Me_2(NEt_2)_4$.[34-36] $M_2(OR)_6$ compounds react reversibly with CO_2 to give $M_2(OR)_4(O_2COR)_2$ compounds.[22,26,27,38] Reactions involving CS_2 and COS also give products of M-N or M-O bond insertion, but these have not yet been properly characterized. Insertions into M-C bonds have not been observed.

All of the aforementioned compounds are diamagnetic crystalline solids with appreciable solubilities in hydrocarbon solvents. They are all sensitive to oxygen and moisture but quite thermally stable.

Many may be sublimed and all (with the exception of $M_2(OR)_4(O_2COR)_2$ compounds which readily lose CO_2) give molecular ions in the mass spectrometer. They range in color from pale yellow to dark red but show no absorption maxima in the visible region of spectrum. The color is derived from a tailing of intense U.V. absorptions into the visible region of the electronic spectra.

Solid State Structures

The M_2X_6 compounds all have an ethane-like (D_{3d} symmetry) M_2L_6 core (L=C,N,O). The M-M-L angles are ca. 104^0 and the M-M distances fall in the range 2.167 to 2.30Å. For a given ligand X the W-W distance is longer than the Mo-Mo distance by about 0.08Å. $M_2X_2(NR_2)_4$ compounds, where X=halide or alkyl, adopt closely related structures. In the solid state they have anticonformations: the central $M_2L_2N_4$ core (L=C or halide) belongs to the symmetry group C_{2h}. An ORTEP view of the molecular structure of $W_2Cl_2(NEt_2)_4$ [39] is shown in Figure 1 and is representative of this class of compounds.

All dialkylamido structures have planar nitrogen atoms with the alkyl groups oriented to comprise two sets. Those directed over the M-M bond are termed proximal, those directed away distal. M-M triple bond distances for M_2X_6 and $M_2X_4Y_2$ type compounds are given in Table 1.

In $Mo_2(OSiMe_3)_6(HNMe_2)_2$ [40] and $Mo_2(O_2COBu^t)_2(OBu^t)_4$ [38] there are triple bonds between molybdenum atoms which form four σ-bonds to the ligand atoms. The M-L geometry approximates to a square plane.

$W_2Me_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$ adopt closely related structures having approximate C_{2v} symmetry and provide examples of compounds containing M-M triple bonds (W-W$_{av}$ = 2.275Å) between metal atoms that are coordinated to 5 and 6 ligand atoms, respectively. [36] The central $W_2(O_2C)_6$ skeleton of the $W_2(O_2CNMe_2)_6$ molecule is shown in Figure 2. There are two bridging dialkylcarbamato O_2CNR_2 ligands, and each tungsten atom is at the apex of an irregular pentagonal pyramid. The basal vertices of each pyramid are defined by the two oxygen atoms of the bidentate non-bridging carbamato ligand (W-O$_{av}$ = 2.16Å), one oxygen atom from each of the two

bridging carbamato groups (W-O_{av} = 2.09Å) and either an
oxygen atom from the carbamato ligand (W-O_{av}=2.07Å) in
$W_2(O_2CNMe_2)_6$ or a methyl group (W-C_{av}=2.20Å) in $W_2Me_2(O_2CNEt_2)_4$.
In $W_2(O_2CNMe_2)_6$ the second oxygen atoms from the non-bridging
carbamato ligands,which are axially aligned,coordinate weakly
(W-O_{av}=2.67Å) along an extension of the W-W triple bond.

Remarks on Bonding.

M-M triple bonds have now been found between metal atoms
that are coordinated to either 3, 4, 5 or 6 ligand atoms. Since
the formation of a M-M triple bond requires the use of 3 metal
valence orbitals, the total number of metal valence orbitals
used in bonding may vary from 6 in M_2X_6 compounds to 9 in
$W_2(O_2CNMe_2)_6$. In all the compounds a simple analysis of the
symmetry types of orbitals required to form M-M and M-L bonds
and a consideration of the symmetry properties of the metal val-
ence shell orbitals leads to a satisfactory qualitative formu-
lation of electronic structure.

Consider, for example, the bonding in the molecules
$W_2Me_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$. We may assume that the W≡W
bond is formed primarily by overlap of metal d_{z2} orbitals to
give the σ-component and metal d_{xz} and d_{yz} orbitals to give the
π-components. This is in accord with the assumption originally
made[2] and subsequently supported by SCF X_α calculations[41,42]
for the quadruple bonds in $Re_2Cl_8{}^{2-}$ and $Mo_2Cl_8{}^{4-}$. For the five
quasi-coplanar bonds to the ligands,we may then use the metal
s, p_x, p_y, d_{xy} and $d_{x^2-y^2}$ orbitals. In the case of $W_2(O_2CNMe_2)_6$
tungsten p_z orbitals may be employed to help form the weak
axial W-O bonds.

Such a qualitative picture may be viewed as satisfactory
to the extent that it readily accounts for the observed diamagnetic

nature of the compounds and the short M-M distances which are well below the range for M-M distances in compounds containing Mo-Mo single bonds.[10b] It may also be noted that a triple bond consisting of a σ-component and two equivalent π-components has cylindrical symmetry and imposes no restriction on geometry [c.f. in $Re_2Cl_8^{2-}$ where the eclipsed geometry of the two $ReCl_4$ groups is imposed by the M-M δ bond]. The observed geometries are thus determined by the steric requirements of the ligands. M_2X_6, $M_2X_4Y_2$ (X=R,NR_2, OR and Y = halide or alkyl) and $Mo_2(OR)_6(HNR_2)_2$ compounds adopt staggered geometries because steric repulsive interactions dominate. On the other hand the eclipsed geometries found in $Mo_2(OBu^t)_4(O_2COBu^t)_2$, $W_2Me_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$ are imposed by the bridging O_2COBu^t and O_2CNR_2 ligands.

The detailed electronic structure of Mo_2X_6 compounds was the subject of recent SCW X_α calculations.[43] Here the calculated and observed P.E. spectra were in good agreement.

Dynamical Solution Behavior

Since all the compounds are diamagnetic their dynamical solution behavior is readily investigated by variable temperature nmr spectroscopy. The dialkylamido compounds afford a natural opportunity to examine the diamagnetic anisotropy expected for triple bonds. In acetylenes and cyanides the construction of a molecule that places probe nuclei over, as well as along the axis of the triple bond is a difficult task. For $M_2(NR_2)_6$ and $M_2X_2(NR_2)_4$ molecules the two alkyl groups of each R_2N unit naturally adopt the desired placement. Variable temperature nmr studies show that proximal $\rightleftharpoons$ distal alkyl exchange occurs on the nmr time scale.

This is exemplified by the ^1H nmr spectra obtained for $W_2Cl_2(NEt_2)_4$ shown in Figure 3. At high temperatures, $>130^\circ C$, proximal $\rightleftharpoons$ distal ethyl exchange is rapid on the nmr time scale while at low temperatures, $<-16\ ^\circ C$, proximal and distal resonances are froxen out. Three further points are noteworthy. 1). The high temperature limiting spectrum corresponds to an ABX_3 spectrum and the low temperature limiting spectrum to two ABX_3 spectra. Evidently the mechanism of proximal $\rightleftharpoons$ distal exchange does not remove the diastereotopic nature of the methylene protons. 2). The spectra correspond to the presence of only the _anti_ rotamer in solution. This is the rotamer found in the solid state - see Figure 1. 3). There is a large chemical shift separation between proximal and distal methylene proton resonances, _ca_. 2.5 ppm.* The separation between proximal and distal methylene carbon resonances is much larger, _ca_. 30 ppm.

The variable temperature nmr spectra of $M_2R_2'(NR_2)_4$ compounds, where R=Me, CH_2SiMe_3 and R=Me or Et, are more complex because both _anti_ and _gauche_ rotamers exist in equilibria in solution. A gauche $M_2R_2'(NR_2)_4$ molecule (C_2 symmetry) has two types of NR_2 ligands. Detailed variable temperature ^{13}C nmr studies have been reported for $W_2X_2(NEt_2)_4$ compounds where X=Me,[31] CH_2SiMe_3,[30] Br[30] and I.[30] From these and related studies we have shown that proximal $\rightleftharpoons$ distal alkyl exchange occurs by M-N bond rotations. The compounds $M_2(NR_2)_6$ and $M_2X_2(NR_2)_4$ behave in solution as molecular propellers and are stereochemically correspondent to 1,1,2,2 tetra- aryl substituted ethanes.[44]

For $M_2R_2'(NR_2)_4$ compounds (R´=Me or CH_2SiMe_3 and R=Me or Et) anti-to-gauche isomerization has been monitored and found to occur with an energy of activation of 20 to 24 kcal mol^{-1} depending upon the specific R´ R combination. The detailed mechanism of

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*Since the proximal CH_2 group is not fully over the center of the triple bond and the distal one is closer to the core of zero anisotropy than to the bond axis, this observed shift difference is presumably much smaller than that which would result from the full range of the anisotropy.

anti $\rightleftarrows$ gauche isomerization is not yet known: it is known to be intramolecular however. Future studies of compounds of the type $M_2X(NR_2)_5$ are planned. Here each metal atom is effectively labelled and a distinction between a process involving a simple M-M bond rotation and processes involving intramolecular ligand exchange mechanisms are distinguishable.

One final point worthy of mention concerns the absolute assignment of proximal and distal resonances in $M_2(NR_2)_6$ compounds. In view of the closed shell electronic structure of these molecules we expect the dominant induced magnetic field to be in opposition to the applied field and symmetric about the molecular three fold axis. This will lower the effective magnetic field in the region of the distal alkyl groups and increase it in the region of the proximal alkyl groups, with the result that the signals for distal and proximal resonances (both ^1H and ^{13}C) will lie, respectively, upfield and downfield from the nearly identical positions they would otherwise have had. Experimental support for this line of reasoning is seen in the spectra obtained for $M_2(N\binom{Me}{Et})_6$ compounds. Steric considerations suggest that

$M_2(N\binom{Me}{Et})_6$ compounds would prefer structures with proximal rather than distal methyl groups since this relieves the internal crowding of the molecule, and ^1H nmr studies show that

they also in fact have low field N-Me resonances. Even at high

temperatures when proximal $\rightleftarrows$ distal exchange is rapid $M_2(N\binom{Me}{Et})_6$

compounds show NMe resonances which are deshielded relative

to those found in mononuclear compounds such as $Zr(N\binom{Me}{Et})_4$.

M≡M Bond Strengths

A point of considerable interest in compounds containing
M-M multiple bonds concerns the strength of such bonds. Divergent
estimates have been offered, with no figure strictly derived from
experimental data. Recently, in collaboration with Drs. H.A. Skinner
and J. Connor at the University of Manchester, $D(W≡W)$ in $W_2(NMe_2)_6$
has been estimated from reaction calorimetry. The value,
$D(W≡W)=235\pm15$ kcal mol^{-1}, obtained in this study is larger than
any previously determined value for a homodinuclear bond, c.f.
$D(N≡N)=226$ kcal mol^{-1} in N_2, and comparable to the strongest dinu-
clear bond known, namely, $D(C-O)=256$ kcal mol^{-1} in carbon monoxide.[45]
It is, therefore, not unlikely that the strongest of all chemical
bonds between two atoms may occur in compounds containing metal-
to-metal multiple bonds of high order, since some quadruple bonds
may be even stronger.

REACTIONS

The strength of a chemical bond has no simple correlation
with its reactivity as evidenced by the reactivity of the triple bonds
in acetylene and dinitrogen. The M_2X_6, $M_2X_{6-n}Y_n$ and $Cp_2M_2(CO)_4$
compounds undergo a wide variety of reactions many of which
retain the M-M triple bond.

Ligand Substitution: $M_2X_6 \rightarrow M_2Y_6$. Two types of reactions have been
observed in this category. The first involves reaction of an
M-X bond with an organic substrate containing an active hydrogen
atom and is exemplified by the reaction of $M_2(NMe_2)_6$ compounds
with alcohols which yield $M_2(OR)_6$ compounds with the liberation
of amine. The second is a metathetic reaction of the type
$M_2X_6 + M^1Y \rightarrow M_2X_5Y + M^1X$. An example of this type of reaction is seen
in the formation of $M_2R_2'(NR_2)_4$ compounds from the reaction of
$M_2Cl_2(NR_2)_4$ and LiR' compounds.[30,31] The high reactivity of M-Cl, M-C
(alkyl), M-N(dialkylamido) and M-O(alkoxy) bonds suggests that other
$M_2X_{6-n}Y_n$ compounds should be synthetically accessible by these
reactions.

We noted that anti-$W_2Cl_2(NEt_2)_4$ reacts stereospecifically
with $LiCH_2SiMe_3$ to give anti-$W_2(CH_2SiMe_3)_2(NEt_2)_4$, which then
slowly isomerizes to the gauche-rotamer: a-$W_2R_2(NEt_2)_4 \rightleftharpoons$ g-$W_2R_2(NEt_2)_4$;
K=4, $30°C$ for R=CH_2SiMe_3.[29,30] This observation strongly supports the
view that (i) the W-W bond is not cleaved during the R-for-Cl
substitution reaction and (ii) alkyl-for-chloro group exchange
proceeds with retention of configuration at tungsten. Rather
interestingly anti-$W_2Cl(CH_2SiMe_3)(NEt_2)_4$ was not detected during
the course of this reaction. Apparently the introduction of one
alkyl group labilizes the second R-for-Cl exchange in the anti
position. This is reminiscent of the high trans-influence and
trans-effect exerted by alkyl ligands in square planar platinum(II)
chemistry,[4,6] though more work needs to be done before any general
conclusions can be reached concerning the substitutional behavior
of $M_2X_{6-n}Y_n$ compounds.

Lewis Base Association

Several $M_2(OR)_6$ compounds react reversibly with donor ligands
L to give adducts $M_2(OR)_6L_2$ where L = an amine or phosphine.
Similarly $Cp_2M_2(CO)_4$ react with phosphines and carbon monoxide
to give $Cp_2M_2(CO)_4L_2$ compounds. In the latter case the M-M bond
order changes from three to one: the Mo-Mo distances
in $Cp_2Mo_2(CO)_4$ and $Cp_2Mo_2(CO)_6$ are 2.40[6] and $3.27Å$,[7] respectively.
No such change accompanies adduct formation with $M_2(OR)_6$ compounds:
the Mo-Mo distances in $Mo_2(OCH_2CMe_3)_6$ and $Mo_2(OSiMe_3)_6(HNMe_2)_2$
are $2.222(1)Å$ and $2.242(1)Å$, respectively.

This striking difference may be accounted for by a consider-
ation of the electronic structure of the M-M triple bonds in these
two classes of compounds. In $Cp_2M_2(CO)_4$ compounds the metal
atoms attain 18-valence shell electron configurations by the
formation of the M-M triple bond. In $M_2(OR)_6$ compounds, where
each metal forms 3 σ-bonds to OR groups and a triple bond to the

other metal atom only a 12-valence shell electron configuration
is achieved. Thus the metal atoms in the dinuclear alkoxides $M_2(OR)_6$
may increase their coordination number without introducing
a significant change in M-M bonding. This point is further illus-
trated by the reactions which lead to alkylcarbonato and dialkyl-
carbamato compounds described below.

Insertion Reactions

M-C(alkyl),[47] M-N(dialkylamide)[33] and M-O(alkoxide)[48] bonds are
known to be labile to a large number of insertion reactions which
may be represented by the general eq. 9

9   M-X + un $\rightleftarrows$ M-un-X
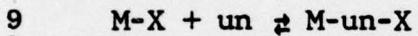
where X = R, NR_2 and OR and un = an unsaturated organic molecule.
Thus far, we have examined in detail only the reactivity of
M_2X_6 compounds toward CO_2. We find that insertion into M-NR_2
and M-OR groups occurs readily, but no reaction is observed for
M-R groups. This is clearly seen in the reaction between
$W_2Me_2(NEt_2)_4$ and CO_2 which gives $W_2Me_2(O_2CNEt_2)_4$.[36]

Insertion into M-NR_2 bonds is irreversible and proceeds via
an amine catalyzed sequence: $HNR_2 + CO_2 \rightleftarrows HO_2CNR_2$; M-$NR_2$ + HO_2CNR_2 →
MO_2CNR_2 + HNR_2.[34] Insertion into M-OR bonds to give $M_2(OR)_4(O_2COR)_2$
compounds is readily reversible and is believed to proceed by a
direct insertion mechanism.[38]

Reductive Elimination

A simple intramolecular reductive elimination of an X-Y group
across a M-M triple bond to yield a compound containing a M-M
quadruple bond has not yet been established. Several of the compounds
described here should serve as excellent models for this type of
reaction. For example, we have found that when $W_2Me_2(O_2CNEt_2)_4$
is heated to above $150^{\circ}C$ ethane is liberated.[12] However, the origin
of the ethane and the nature of the residual tungsten containing
species have still to be determined. An investigation of the

chemistry of molybdenum analogues should be more instructive, since $Mo_2(O_2CR)_4$ compounds (but not $W_2(O_2CR)_4$ compounds) are well known to contain M-M quadruple bonds.[3] In this regard we note that both $Mo_2(CH_2SiMe_3)_6$ and $Mo_2(OPr^i)_6$ react with acetic acid to yield, upon vacuum sublimation, $Mo_2(OAc)_4$.[4,9] Here M-M triple to quadruple bond transformation is achieved, but the detailed reaction pathway and the nature of the eliminated organic compound(s) are not yet known.

Oxidative-Addition

The addition of an X-Y substrate across a M-M triple bond might be expected to yield a compound containing a M-M double bond: $L_nM \equiv ML_n + X-Y \rightarrow L_nXM = MYL_n$. This transformation has yet to be established structurally, although there are a number of reactions such as, $Cp_2M_2(CO)_4 + I_2 \rightarrow Cp_2M_2(CO)_4I_2$,[6] in which this might occur. However, an anticipated oxidative addition to a M-M multiple bond may change the M-M bond order by more than one unit. For example, addition of X_2 (X=I or Br) to $Mo_2(S_2COEt)_4$, which contains a M-M quadruple bond, yields $Mo_2X_2(S_2COR)_4$ compounds having Mo-Mo single bonds (Mo-Mo=2.72Å) as a result of a surprising rearrangement in the bonding mode of the xanthate ligand.[50] It is also possible that addition may cause complete rupture of the M-M bond:

$Mo_2(NMe_2)_6 + 2Me_2N. \rightarrow 2Mo(NMe_2)_4$.
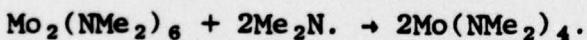
Clearly the reactivity of compounds containing M-M multiple bonds towards reductive-elimination and oxidative-addition reactions is going to be as complex and is at present even less predictable than analogous reactions involving mononuclear transition metal complexes.[51,52]

Reactions of the M-M Triple Bond with Small Unsaturated Molecules

$Cp_2M_2(CO)_4$ compounds react in solution under very mild conditions with a large number of unsaturated organic molecules, un, to form 1:1 adducts $Cp_2M_2(CO)_4$(un). The compounds where M = Mo and un = $PhC \equiv CPh$, $EtC \equiv CEt$, $HC \equiv CH$, $CH_2=C=CH_2$ and Me_2NCN have been

characterized by X-ray crystallography.[53-56] In all cases un acts as a four electron donor ligand and spans the Mo_2 bond which increases in length from 2.40Å in $Cp_2Mo_2(CO)_4$ to 2.974, 3.015 and 3.117Å when un = HC≡CH, Me_2NCN and $CH_2=C=CH_2$, respectively.

The acetylene adducts share a common $Cp_2Mo_2(CO)_4C_2$ structure which is shown in Figure 4. There is a cross-wise acetylene bridge (i.e, a psuedo-tetrahedral Mo_2C_2 core), typical of that found in many other dinuclear acetylene complexes.[57-62] The asymetry of the $Cp_2Mo_2(CO)_4$ moiety presumably arises from internal steric crowding. In the adducts where un=Me_2NCN and $CH_2=C=CH_2$, the $Cp_2Mo_2(CO)_4$ moiety adopts a more relaxed structure having virtual C_2 symmetry.

Allene bridges the Mo-Mo bond obliquely. One of the allenic-π-orbitals donates a pair of electrons to one molybdenum atom while the other orthogonal allenic-π-orbital interacts with the other molybdenum atom. The bonding of the dimethylcyanimide molecule to the Mo_2 group is schematically shown below.

$$
\begin{array}{c}
\text{Me} \quad \text{Me} \\
\diagdown \quad \diagup \\
\text{N} \\
| \\
\text{C} \\
\| \\
\text{N} \\
\diagup \quad \diagdown \\
\text{Mo} \text{——} \text{Mo}
\end{array}
$$
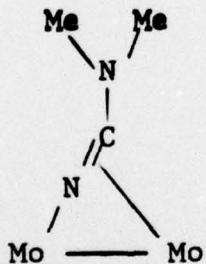
The central NCN angle is 135° and the five non-hydrogen atoms of the Me_2NCN moiety lie in a plane. The bridging Me_2NCN group thus donates a nitrogen lone pair to one molybdenum atom and a CN π-electron pair to the other one.

$Cp_2M_2(CO)_4$ and $Mo_2(OPr^i)_6$ react with nitric oxide (2 equiv) to yield $2CpMo(CO)_2NO$[63] and $[Mo(OR)_3NO]_2$[64] compounds, respectively. The structure of the isoproxy compound $[Mo(OPr^i)_3NO]_2$ has been determined by X-ray crystallographic studies:[64] the immediate coordination about the metal atoms in this centrosymmetric molecule is

shown in Figure 5.   Each molybdenum atom is in a trigonal bi-
pyramidal environment having a terminal NO and a long Mo-O bond
of a bridging OPr^i ligand in the axial positions. The Mo-Mo
separation of 3.335(2)Å signifies an absence of metal-to-metal bonding.

In a formal sense, these reactions of M-M triple bonds with
NO to give two Mo-NO groups correspond to the replacement of the
Mo≡Mo bond (a σ-bond plus two π-bonds) by two Mo≡N-Ö: bonds.
Again, there is a σ-electron pair and two π-electron pairs shared
by the Mo atom and its partner, which is now a nitrogen atom
instead of another molybdenum atom. The low values of υ(NO) in
$[Mo(OR)_3NO]_2$ compounds, ca. 1630 cm^{-1}, are indicative of extensive
molybdenum to NO π* bonding.

The dinuclear alkoxides are also extremely reactive towards
carbon monoxide and acetylenes. With two equivalents of CO,
$Mo_2(OPr^i)_6$ yields a polymeric black crystalline compound of empirical
formula $Mo(OPr^i)_3(CO)$ which shows υ(CO) at 1960, 1880, 1840 and
1820 cm^{-1}. Upon heating in vacuo, this compound, yields $Mo(CO)_6$
and $Mo_2(OPr^i)_8$ by sublimation and an as yet uncharacterized
residue.

Polynuclear Complexes

The factors which lead to the formation of dinuclear compounds
containing M-M bonds of multiple order n rather than to the
formation of polynuclear or cluster compounds in which the metal
atoms form n σ-bonds with each other are not well understood.
The size of the ligands is one important factor and this is
illustrated in the following.

Alkoxides of Mo(III) and W(III) exist in the dinuclear M-M
triple-bonded form only when the R group is bulky. For molybdenum,
the neopentoxide exists in both   dinuclear and polymeric forms.
The ethoxide is tetrameric and diamagnetic in solution and shows

ions $Mo_4(OEt)_{12}^+$, $Mo_3(OEt)_9^+$ and $Mo_2(OEt)_6^+$ in the mass spectrum.[27] For tungsten only the very bulky triethylsiloxy and tertiary butoxy ligands give dinuclear compounds.[22] The less bulky isopropoxy and neopentoxy groups give tetranuclear complexes. A black crystalline tetranuclear compound $W_4(OPr^i)_{12}(HOPr^i)_2$ has been structurally characterized (See Fig. 6) and is believed to have one of the two Pr^iOH ligands coordinated at each terminal tungsten.[65] Formation of $W_4(OPr^i)_{12}(HOPr^i)_2$ may be viewed as the first step in a polymerization of $W_2(OPr^i)_6$ which is halted in this instance by the coordination of the Pr^iOH ligands.

Since the chloro ligands in $M_2Cl_2(NR_2)_4$ compounds are sub-stitutionally labile, reactions involving organometallic anions might allow for the synthesis of new polynuclear and cluster compounds incorporating the unsaturated M_2 moiety. This is an area of current investigation.

Potential Catalytic Reactions

The ability of compounds containing M-M triple bonds to enter into reactions well documented in mononuclear organometallic chemistry suggests that they may prove of catalytic significance. Indeed, one catalytic sequence (Eq. 10) is already suggested by the ability of the $Cp_2M_2(CO)_4$ compounds to coordinate unsaturated molecules that are four- but not two-electron donors.

(i) $Cp_2M_2(CO)_4 + un \rightarrow Cp_2M_2(CO)_4(un)$

10

(ii) $Cp_2M_2(CO)_4(un) + H_2 \rightarrow Cp_2M_2(CO)_4 + unH_2$
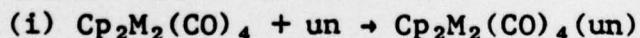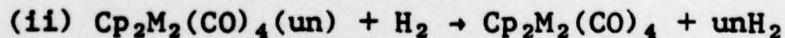
Our attempts to hydrogenate the acetylene in $Cp_2Mo_2(CO)_4(HC_2H)$ in benzene at 25 and $70°C$ proved unsuccessful, though at $100°$ ethylene is apparently formed.[66] The potential of $Cp_2M_2(CO)_4$ compounds for selective hydrogenation catalysis should be examined further.

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Captions to Figures

Fig. 1   An ORTEP view of the $W_2Cl_2(NEt_2)_4$ molecule in which each atom is represented by its ellipsoid of thermal vibration drawn to enclose 50% of the electron density.

Fig. 2   The central $W_2(O_2C)_6$ skeleton of the $W_2(O_2CNMe_2)_6$ molecule. The dotted lines indicate the long, quasi-axial W-O bonds.

Fig. 3 ^1H nmr spectra of $W_2Cl_2(NEt_2)_4$ in toluene-d_8 recorded at 100 MHz. Top at +150°C, bottom at -18°C corresponding to fast and slow proximal ⇌ distal exchange spectra on the nmr time scale, respectively.

Fig. 4   An ORTEP view of the $Cp_2Mo_2(CO)_4C_2$ skeleton found in the acetylene adducts $Cp_2Mo_2(CO)_4(RCCR)$ where R=H, Et and Ph.

Fig. 5   An ORTEP view of the $[MoO_3NO]_2$ skeleton of the $[Mo(OPr^i)_3NO]_2$ molecule showing the coordination geometry about molybdenum and average bond distances. The Mo---Mo distance is 3.335(1)Å.

Fig. 6   An ORTEP view of the $W_4(OPr^i)_{12}(HOPr^i)_2$ molecule showing only the W_4O_{14} skeleton. The molecule has C_1 symmetry. Some important parameters are: W(1)-W(2)=2.46Å; W(1)-W(1)ʹ=3.30Å; W(2)-W(1)-W(1)ʹ angle=140°.

Fig. 1.

Fig. 2

150°

−18°

6.0   5.0   4.0   3.0   2.0   1.0   0.0   ppm (δ)
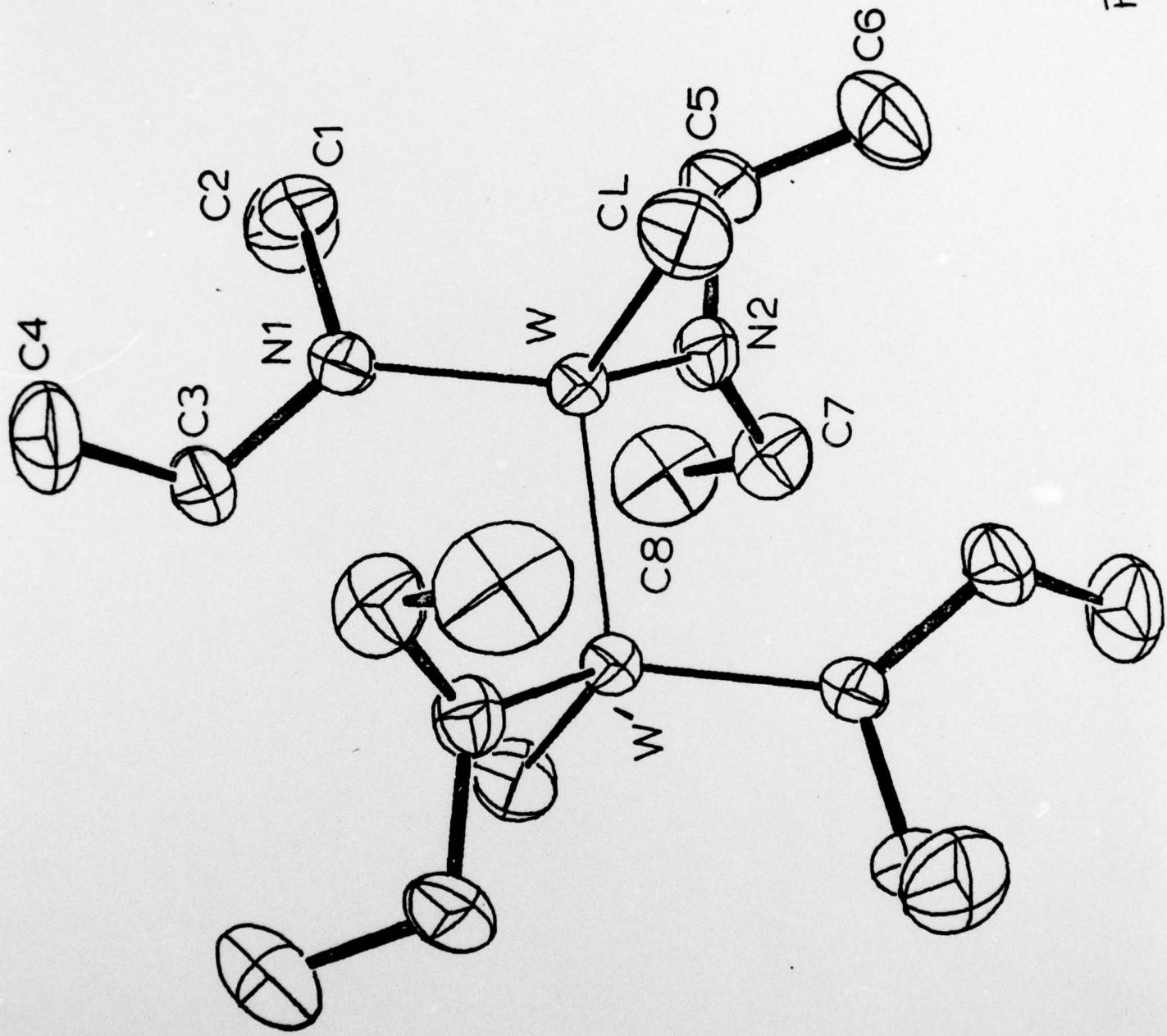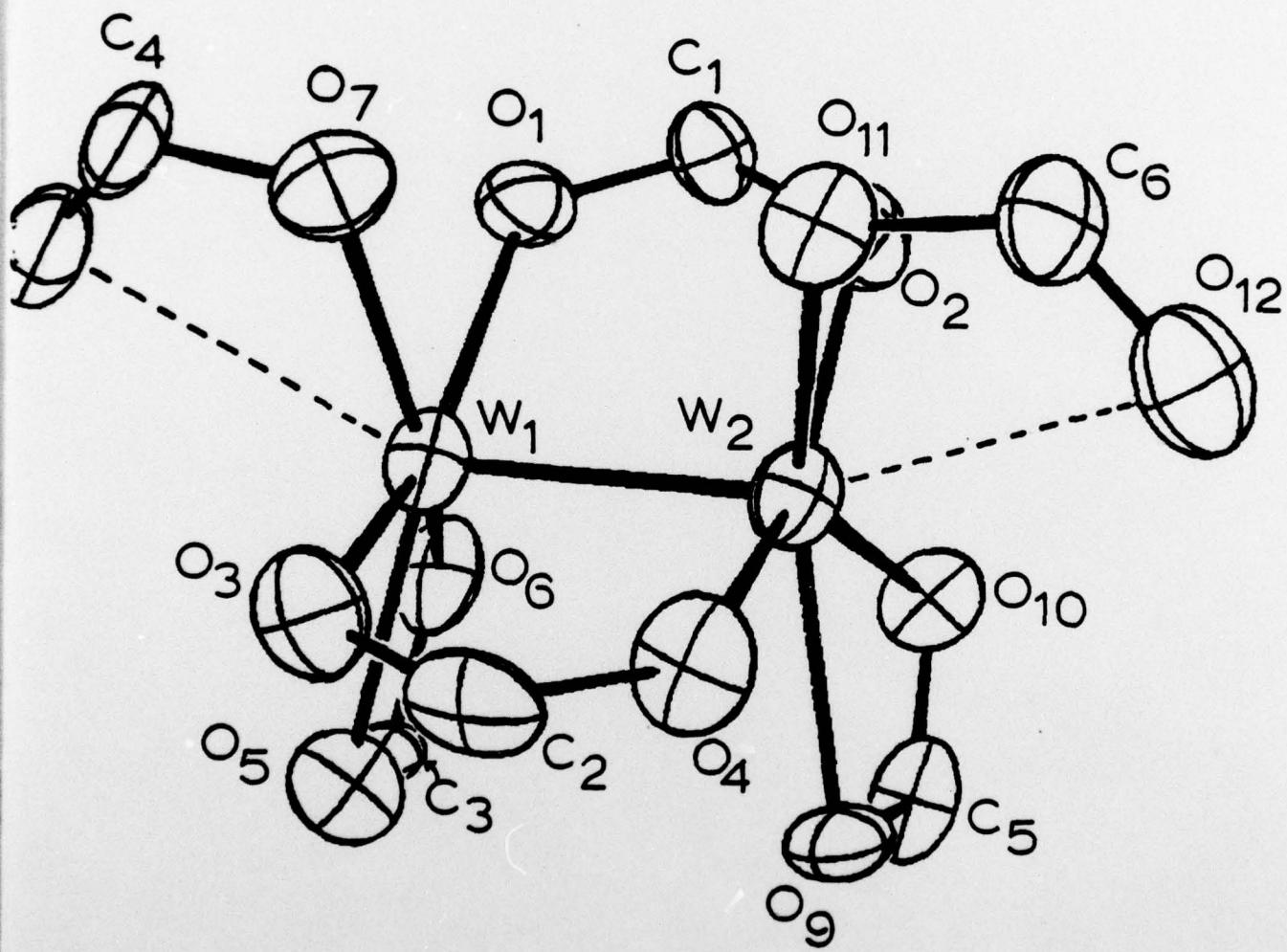
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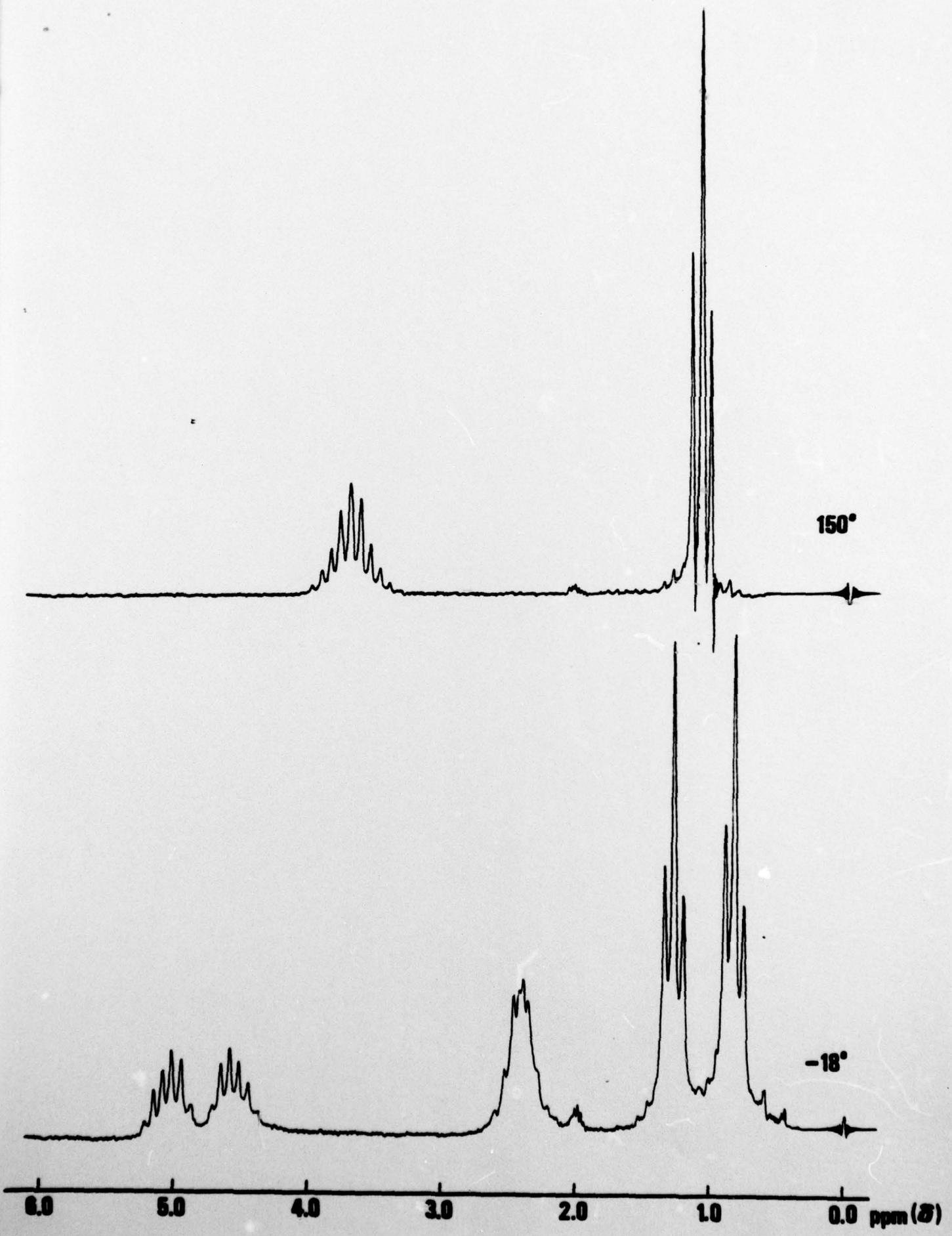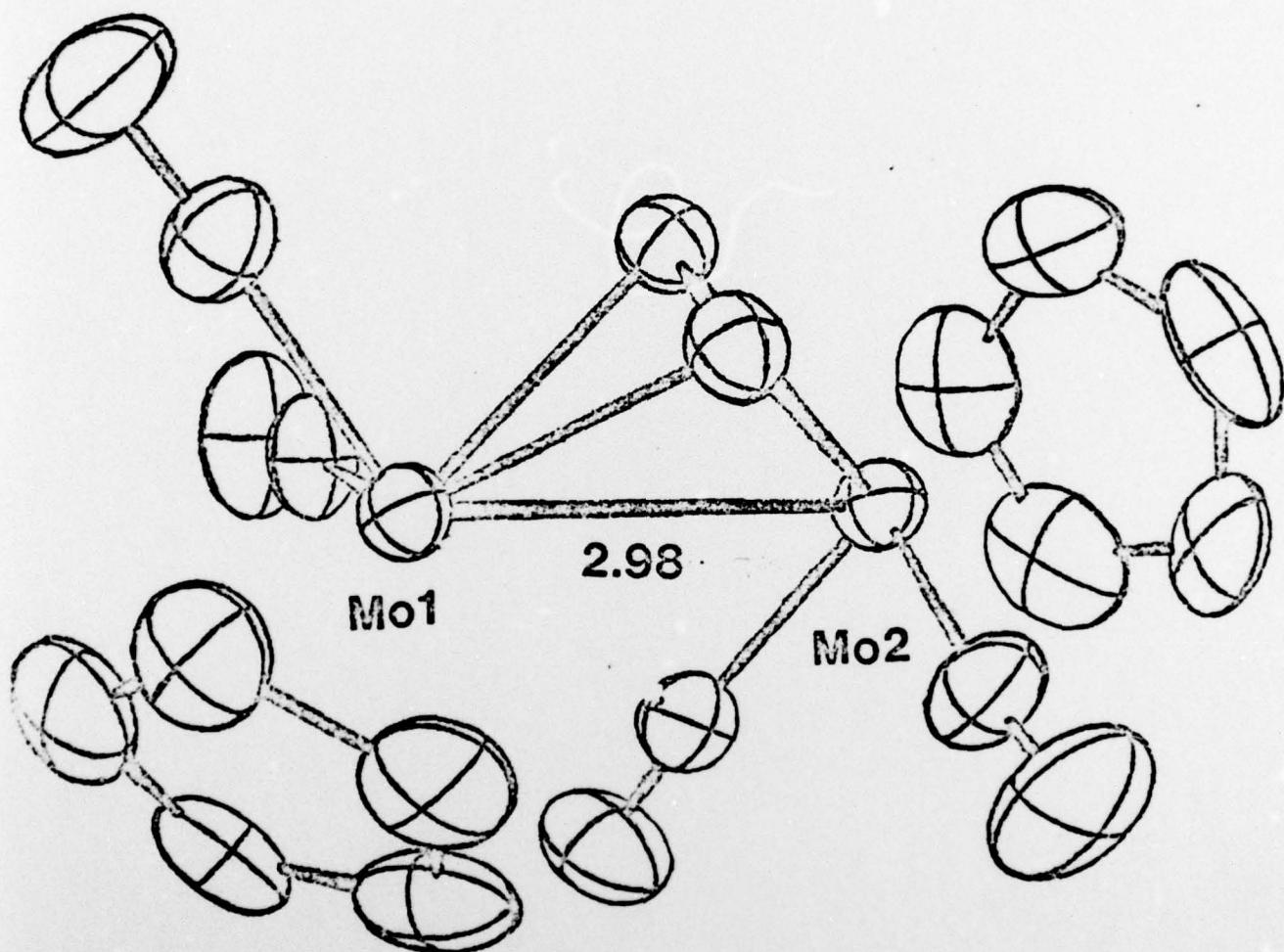
Fig. 4.
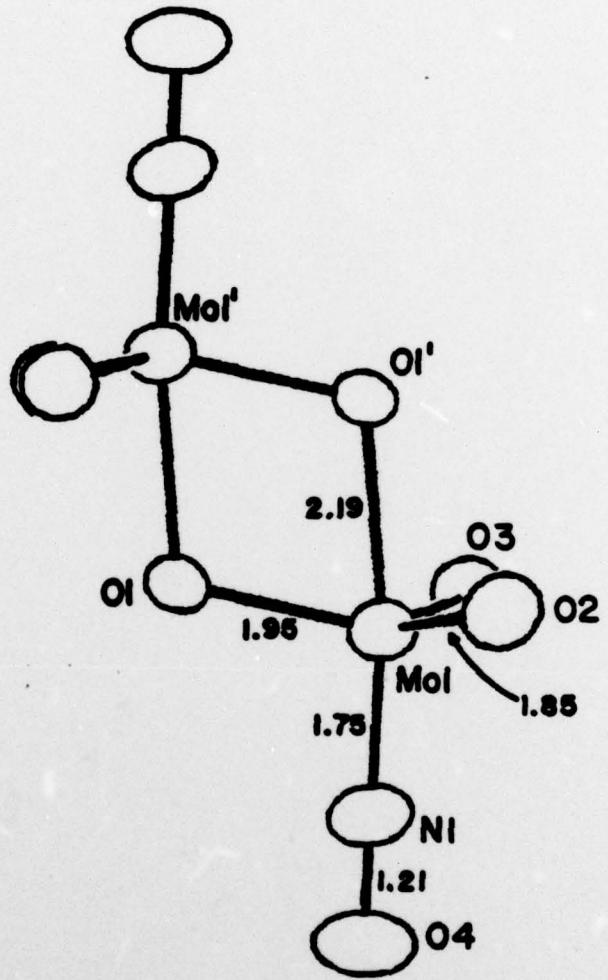
Fig 5

Fig. 6
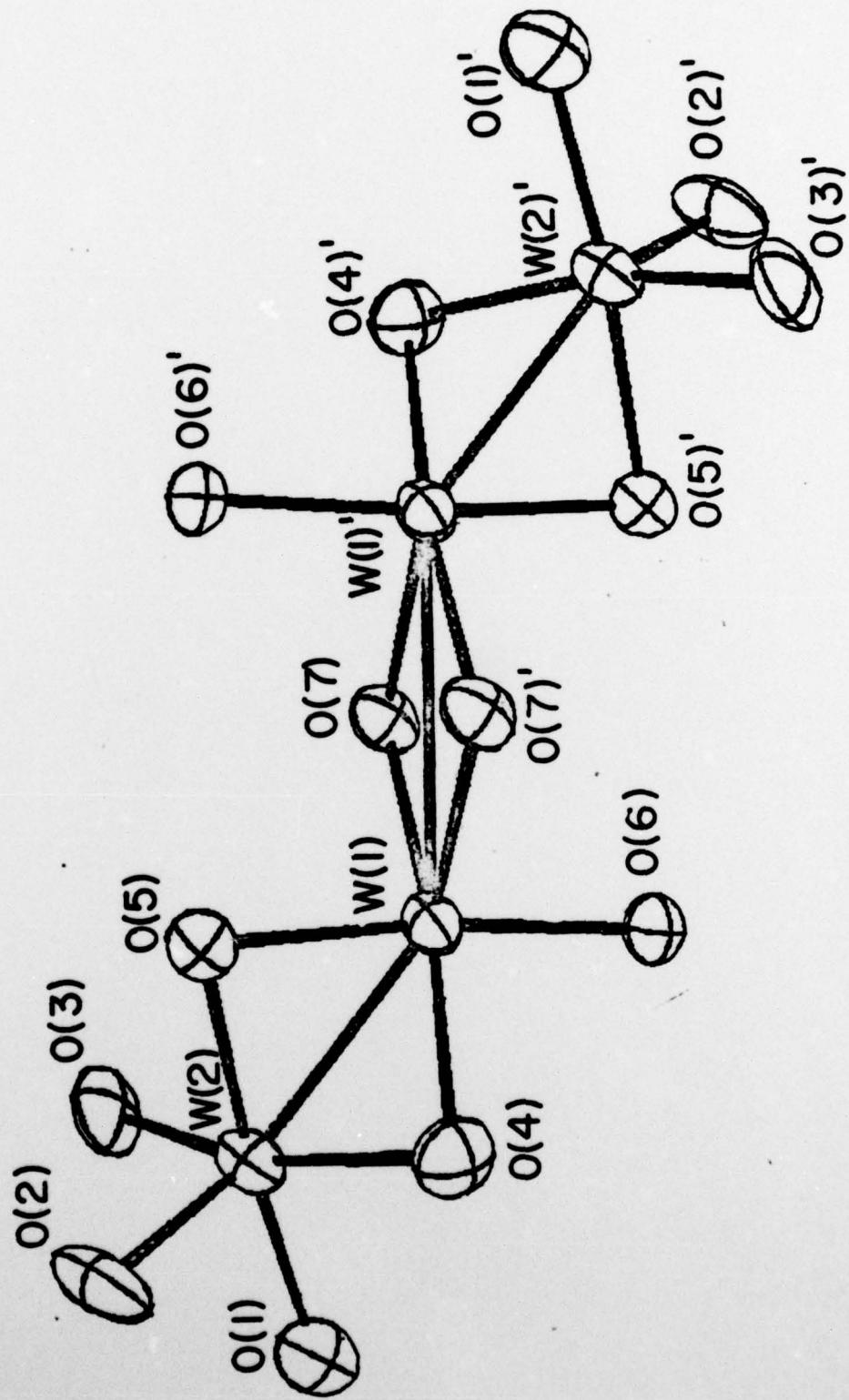
Table 1.   M-M Triple Bond Distances in M_2X_6 and $M_2X_2Y_4$ Compounds

Compounds	M-M Å
$Mo_2(CH_2SiMe_3)_6$	2.167(?)
$W_2(CH_2SiMe_3)_6$	2.255(2)
$Mo_2(NMe_2)_6$	2.214(3)
$W_2(NMe_2)_6$	2.294(2)
$Mo_2(OCH_2CMe_3)_6$	2.222(2)
$Mo_2Cl_2(NMe_2)_4$	2.201(2)
$W_2Cl_2(NMe_2)_4$	2.285(2)
$W_2Cl_2(NEt_2)_4$	2.301(1)
$W_2Br_2(NEt_2)_4$	2.301(2)
$W_2I_2(NEt_2)_4$	2.300(4)
$W_2Me_2(NEt_2)_4$	2.291(1)
$Mo_2Me_2(NMe_2)_4$	2.201(1)
$Mo_2(OBu^t)_4(O_2COBu^t)_2$	2.241(1)
$Mo_2(OSiMe_3)_6(HNMe_2)_2$	2.242(1)
$W_2Me_2(O_2CNEt_2)_4$	2.272(1)
$W_2(O_2CNMe_2)_6$	2.279(1)

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